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⑤④ A process for preparing 1,7-octadiene.

⑤⑦ A process for hydrodimerizing butadiene to form 1,7-octadiene in high selectivity comprises hydrodimerizing butadiene in the presence of a palladium catalyst, a tertiary phosphine, formic acid, a solvent and in the absence of a base, characterized in that the solvent is a dialkyl sulphoxide and/or a dialkyl formamide and the tertiary phosphine is a phosphine of formula:



wherein R<sub>1</sub> is a benzyl group or a branched alkyl, alkenyl, aralkyl or cycloalkyl group having from 3 to 10 carbon atoms with branching occurring at a carbon atom no more than two carbon atoms from the phosphorous atom and R<sub>2</sub> and R<sub>3</sub> are R<sub>1</sub> or independently are alkyl, alkenyl or aryl having from 1 to 10 carbon atoms.

**EP 0 008 139 A1**



## A PROCESS FOR PREPARING 1,7-OCTADIENE

The present invention is concerned with a process for preparing 1,7-octadiene by hydrodimerizing butadiene in the presence of a catalytic amount of palladium, a tertiary phosphine, formic acid and a solvent.

5        Linear dimerization of butadiene (1,3-butadiene) provides a source of  $C_8$ -unsaturated hydrocarbon intermediates useful for the synthesis of diacids, diesters, diols or diamines. A particularly preferred dimer is 1,7-octadiene which has terminal double bonds and allows the production of product having only terminal functional  
10 groups.

U.S. Patent Specification No. 3,732,328 discloses the preparation of mixtures of octadienes, primarily 1,6-octadiene, by reacting butadiene in the presence of a palladium compound, formic acid, a polar solvent, a reducing agent and a tertiary phosphine.  
15 Trialkyl, mixed alkylaryl or triaryl phosphines are mentioned as useful, specifically noting triphenyl phosphines. The yield of 1,7-octadiene is much lower than that of the present invention.

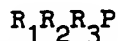
Tetrahedron Letters No. 2, pp. 163-164 discloses the production of mixtures of octadienes by reacting butadiene in  
20 the presence of palladium acetate, triphenyl phosphine formic acid and dimethyl formamide. The yield of 1,7-octadiene is much lower than that of the present invention.

Our co-pending Patent Application No. 79200141.4 discloses the production of 1,7-octadiene by reacting butadiene in the presence  
25 of a palladium catalyst, tri-isopropyl phosphine, formic acid, a base and optionally a solvent. The present invention in contrast operates without the presence of a base.

The process of the present invention is concerned with the hydrodimerization of butadiene to 1,7-octadiene in high selectivity  
30 by hydrodimerizing butadiene in the presence of a palladium catalyst, a tertiary phosphine, formic acid, a solvent and in the



absence of a base, characterized in that the solvent is a dialkyl sulphoxide and/or a dialkyl formamide and the tertiary phosphine is a phosphine of formula:



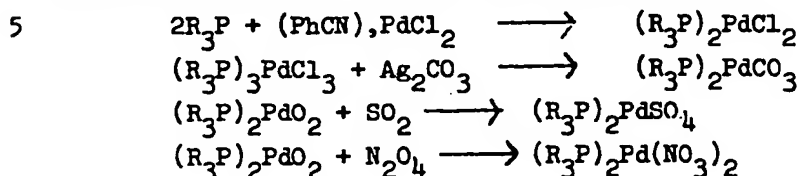
- 5 wherein  $R_1$  is a benzyl group or a branched alkyl, alkenyl, aralkyl or cycloalkyl group having from 3 to 10 carbon atoms with branching occurring at a carbon atom no more than two carbon atoms from the phosphorus atom and  $R_2$  and  $R_3$  are  $R_1$  or independently are alkyl, alkenyl or aryl having from 1 to 10  
10 carbon atoms.

If the palladium compound added is a palladium tertiary phosphine complex then it is not necessary to add a separate tertiary phosphine. The use of the tertiary phosphine in combination with the solvents of this invention allows the hydro-  
15 dimerization reaction to be carried out in high yield without a base being required.

The catalyst used in the process of this invention is palladium or a palladium compound complexed with a tris-organo phosphine. The palladium may be in any of its possible  
20 valence states, e.g., 0, +2, etc. Suitable palladium compounds include the palladium carboxylates, particularly palladium carboxylates derived from alkanolic acids containing up to six carbon atoms, such as palladium acetate, complexes, such as palladium acetyl acetonate, bis-benzonitrile palladium(II)  
25 and lithium palladous chloride as well as the palladium halides, nitrates and sulphates, such as palladous chloride, palladium nitrate ( $Pd(NO_3)_2(OH)_2$ ) and palladium sulphate. Preferred catalysts are palladium acetyl acetonate or palladium acetate. Suitable reduced palladium-phosphine complexes are  
30  $Pd(R_3P)_2$  or  $Pd(R_3P)_3$ . A preferred complex is  $Pd(0)$ -tri-isopropyl phosphine. The palladium is present in the reaction mixture in catalytic amounts; preferably from about 1 to about  $10^{-6}$  molar and more preferably from about  $10^{-1}$  to about  $10^{-4}$  molar.



The palladium compounds complexed with a tris-organo phosphine are typically prepared by reacting the tertiary phosphine with the appropriate palladium compound as, for example, represented by the following equations:

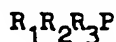


where  $R_3P$  is the tris-organo phosphine of the invention, or  
 10 may be made in situ by adding the palladium compound and the phosphine directly to the reactor.

The catalyst may be pretreated to enhance reactivity by contacting it with a reducing agent at a temperature of from about 20 to about 90°C for from about 0.1 to about 5 hours.

15 The reducing agent may be gaseous, solid or liquid. Examples of gaseous agents are hydrogen and carbon monoxide. Examples of liquid or solid reducing agents are hydrazine,  $NaBH_4$ ,  $NaOCH_3$ , (isopropyl) $_3P$ , Cu, Na and alkyls, etc. The reduction may be carried out in a separate autoclave or preferably is carried  
 20 out in the hydrodimerization reactor prior to the introduction of the butadiene. The palladium compound-tri-organo phosphine complex may be dissolved in the solvent used in this invention prior to reduction.

The tris-organo phosphines utilized in the process of this  
 25 invention have the following general formula:



wherein  $R_1$  is a benzyl group or a branched alkyl, aralkyl, alkenyl or cycloalkyl group having from 3 to about 10 carbon atoms with branching occurring at a carbon atom no more than  
 30 two carbon atoms from the phosphorus atom and  $R_2$  and  $R_3$  are  $R_1$  or independently are alkyl, alkenyl or aryl groups having from 1 to about 10 carbon atoms.

By branched is meant that the  $\alpha$ - and  $\beta$ -carbon atoms, relative to the phosphorus atom, of the stated groups may not  
 35 both be  $-CH_2$ -linkages.



Illustrative of the  $R_1$  moiety are, for alkyl, isopropyl, sec.-butyl, tert.-butyl, isobutyl, neopentyl, sec.-pentyl, tert.-pentyl, 2-methylbutyl, sec.-hexyl, tert.-hexyl, 2-2-dimethylpropyl; for aralkyl, alpha-methylbenzyl, alpha,alpha-dimethylbenzyl, alpha-methyl-alpha-ethylbenzyl, phenylethyl, 5 phenylisopropyl, phenyl-tert.-butyl; for cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the like.

Illustrative of  $R_2$  and  $R_3$  are, for example, methyl, ethyl, 10 propyl, butyl, pentyl, hexyl, octyl, nonyl and decyl for alkyl; allyl, crotyl and methallyl for alkenyl and phenyl, tolyl, xylyl, ethylphenyl, propylphenyl for aryl. Two or more of the instant phosphines may be used in the same reaction or another phosphine may be replaced by reacting in situ one of the instant 15 phosphines. Preferred phosphines are tri-isopropyl phosphine, tri-cyclohexyl phosphine, tri-tert.-butyl phosphine, tri-sec.-butyl phosphine, di-tert.-butyl-normal-butyl phosphine, and tri-isobutyl phosphine, dicyclohexylalkyl phosphine, di-(tert.-butyl)alkyl phosphine, di(tert.-butyl)alkenyl phosphine, tert.-butyldibenzyl 20 phosphine, tert.-butyldialkyl phosphine and mixtures thereof.

The mol. ratio of tris-organo phosphine to palladium is at least 1. Preferably, the mol. ratio of phosphine to palladium ranges from about 1:1 to about 20:1 and preferably from about 2:1 to about 5:1.

25 The solvents needed to provide the high yields of this invention are selected from the group consisting of dialkyl sulfoxides and dialkyl formamides. The alkyl moieties have carbon numbers ranging from 1 to about 6. Included within the definitions of dialkyl would be polyalkylene, e.g., an alkyl 30 group doubly attached to the sulfoxide or formamide group as, for example, tetramethylene sulfoxide, N-methyl pyrrolidinone. Preferred solvents are dimethyl sulfoxide and dimethyl formamide.



The addition of carbon dioxide to the reaction system has been found to increase the extent of butadiene conversion, but does not affect the selectivity. When it is desired to use carbon dioxide to increase the conversion rate, the partial  
5 pressure of the  $\text{CO}_2$  in the reaction system may be from about 0.5 to about 70 bars. Since carbon dioxide is a by-product of the process, it is possible to generate sufficient carbon dioxide in situ to enhance the conversion rates.

The process can be either continuous or batch. The re-  
10 action temperature of the process is not critical, however, it is preferred to maintain the reaction between about 0 to about  $100^\circ\text{C}$ , preferably between about 20 to about  $70^\circ\text{C}$ . The process is conducted at the reaction temperature. Typically the pressure is autogeneous.

15 The process of this invention is particularly useful when applied to a butadiene/isobutane/n-butenes (BBB) stream from an oil pyrolysis unit. These BBB streams are the  $\text{C}_4$  cut from a thermal cracking unit typically containing 30-40% butadiene, 20-35% isobutene and 20-30% n-butenes and many other minor  
20 components.

The process of this invention will now be illustrated by reference to the following Examples.

#### EXAMPLE 1

To an 80 ml glass-lined autoclave were charged  $2.7 \times 10^{-5}$   
25 moles of the palladium compound listed in column 1 of Table I,  $5.4 \times 10^{-5}$  moles of tri-isopropyl phosphine,  $1.85 \times 10^{-2}$  moles of formic acid, 2 g of butadiene and 10 ml of the solvent listed in column 2 of Table I. The stirred reactor was heated to  $60^\circ\text{C}$  for 1 hour. The reactor was then cooled and the product  
30 was analyzed by gas chromatography. The results are shown in column 3 of Table I.



TABLE I

Pd compound	Solvent	Butadiene conversion to 1,7-octadiene, %
Pd(AcAc) <sub>2</sub> <sup>a)</sup>	Dimethyl sulphoxide	77
Pd(AcAc) <sub>2</sub>	Tetramethylene sulphoxide	83
Pd(AcAc) <sub>2</sub>	Dimethyl formamide	98
5 Pd(AcAc) <sub>2</sub>	N-methyl pyrrolidinone	75
Pd(AcAc) <sub>2</sub>	Dimethyl acetamide	70
Pd(AcAc) <sub>2</sub>	Pyridine	30
Pd(AcAc) <sub>2</sub>	Tetrahydrofuran	24
Pd(AcAc) <sub>2</sub>	Quinoline	17
10 Pd(AcAc) <sub>2</sub>	Sulfolane	3
Pd(AcAc) <sub>2</sub>	Nitromethane	0
Pd(AcAc) <sub>2</sub>	Ethyl sulphide	0
Pd(AcAc) <sub>2</sub>	None	0
Pd(OAc) <sub>2</sub> <sup>b)</sup>	Dimethyl sulphoxide	78
15 Pd(OAc) <sub>2</sub>	Dimethyl formamide	66
Pd(OAc) <sub>2</sub>	N-methyl pyrrolidinone	40
Pd(OAc) <sub>2</sub>	2,6-lutidine	35
Pd(OAc) <sub>2</sub>	Dimethyl acetamide	4.5
Pd(OAc) <sub>2</sub>	Acetamide	0.8
20 Pd(OAc) <sub>2</sub>	Formamide	0
Pd(OAc) <sub>2</sub>	Acetonitrile	0
Pd(OAc) <sub>2</sub>	Dimethyl aniline	0
PdSO <sub>4</sub>	Dimethyl sulphoxide	68
PdSO <sub>4</sub>	Dimethyl formamide	98
25 PdSO <sub>4</sub>	Pyridine	18
PdSO <sub>4</sub>	Tetrahydrofuran	9
Pd(NO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Dimethyl sulphoxide	21
Pd(NO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	Dimethyl formamide	2
PdCl <sub>2</sub>	Dimethyl formamide	0.9
30 Pd( $\phi_3$ P) <sub>4</sub> <sup>c)</sup>	Dimethyl formamide	0.3

<sup>a)</sup> AcAc = acetyl acetate; <sup>b)</sup> OAc = acetate;

<sup>c)</sup> No (Isopropyl)<sub>3</sub>P added;  $\phi_3$ P represents triphenyl phosphine.



EXAMPLE 2

To an 80 ml glass-lined autoclave were charged  $2.5 \times 10^{-5}$  moles of the palladium compound listed in column 1 of Table II,  $5.4 \times 10^{-5}$  moles of tri-isopropyl phosphine,  $1.85 \times 10^{-2}$  moles of formic acid, 2 g of butadiene and 10 ml of the solvent listed in column 2 of Table II. The stirred reactor was heated to  $40^{\circ}\text{C}$  for 2 hours. The reaction was then cooled and the product was analyzed by gas chromatography. The results are shown in columns 3 and 4 of Table II. Tri-isopropyl phosphine and triphenyl phosphine are abbreviated by  $i\text{-Pr}_3\text{P}$  and  $\phi_3\text{P}$ .

TABLE II

Pd compound	Solvent	Other changes	Conversion to 1,7-octa- 1,6-octa- diene, % diene, %	
$\text{Pd}(\text{AcAc})_2$	Dimethyl formamide		55.0	1.0
$\text{Pd}(\text{AcAc})_2$	Dimethyl formamide	No P	5.8	43.0
$\text{Pd}(\text{AcAc})_2$	Dimethyl formamide	$\phi_3\text{P}$ in place of $i\text{-Pr}_3\text{P}$	5.8	0.9
$\text{Pd}(\text{AcAc})_2$	Dimethyl formamide	(Cyclohexyl) $_3\text{P}$ in place of $i\text{-Pr}_3\text{P}$	18.0	0.6
$\text{Pd}(\text{AcAc})_2$	Dimethyl sulphoxide		81.0	2.0
$\text{Pd}(\text{AcAc})_2$	Dimethyl sulphoxide	(Cyclohexyl) $_3\text{P}$ in place of $i\text{-Pr}_3\text{P}$	53.0	2.0
$\text{Pd}(\text{AcAc})_2$	N-Me pyrro- lidinone		40.0	
$\text{Pd}(\text{AcAc})_2$	Pyridine		0.6	
$\text{Pd}(\text{OAc})_2$	Dimethyl formamide		92.0	4.0
$\text{PdSO}_4$	Dimethyl formamide		37.0	
$\text{Pd}(\text{NO}_3)_2(\text{OH})_2$	Dimethyl formamide		0.4	



EXAMPLE 3

To an 80 ml glass-lined autoclave were charged  $2.7 \times 10^{-5}$  moles of palladium acetylacetonate,  $5.4 \times 10^{-5}$  moles of the phosphine listed below, 10 ml of dimethylsulphoxide,  $1.85 \times 10^{-2}$  moles of formic acid and 2 g of butadiene. The stirred reactor was heated to  $40^{\circ}\text{C}$  for 2 hours. The reactor was then cooled and the product was analyzed by gas chromatography. The results are shown in Table III.

TABLE III

10	Phosphine	1,7 octadiene	
		Conversion, %	Selectivity, %
	(isopropyl) <sub>3</sub> P	81	97.5
	(cyclohexyl) <sub>3</sub> P	54	97
	(t-butyl) <sub>2</sub> -n-butyl-P	39	99
	(sec.-butyl) <sub>3</sub> P	20	98.5
15	(t-butyl) <sub>3</sub> P	66	98.5
	(n-butyl) <sub>3</sub> P	9.5	86
	(n-propyl) <sub>3</sub> P	4.0	87
	(ethyl) <sub>3</sub> P	6	85
	(phenyl) <sub>3</sub> P	5.7	86

20 EXAMPLE 4

A zero-valent palladium complex was prepared according to the teachings of W. Kuran and A. Musco, Inorganic Chimica Acta, Vol. 12, 1975, pp 187-193.  $6.8 \times 10^{-6}$  moles of Pd(o)-(tert.-isopropyl phosphine)<sub>3</sub> complex,  $1.85 \times 10^{-2}$  moles of formic acid, 10 ml of dimethyl sulphoxide and 2 g of butadiene were charged to an 80 ml glass-lined autoclave. The stirred reactor was heated to  $60^{\circ}\text{C}$  for one hour, cooled and the product analyzed by gas chromatography. Conversion of butadiene to 1,7-octadiene was 80.4% in 97.3% selectivity.



C L A I M S

1. A process for preparing 1,7-octadiene by hydrodimerizing butadiene in the presence of a palladium catalyst, a tertiary phosphine, formic acid, a solvent and in the absence of a base, characterized in that the solvent is a dialkyl sulphoxide and/or a dialkyl formamide and the tertiary phosphine is a phosphine of formula:
- $$\text{R}_1\text{R}_2\text{R}_3\text{P}$$
- wherein  $\text{R}_1$  is a benzyl group or a branched alkyl, alkenyl, aralkyl or cycloalkyl group having from 3 to 10 carbon atoms with branching occurring at a carbon atom no more than two carbon atoms from the phosphorous atom and  $\text{R}_2$  and  $\text{R}_3$  are  $\text{R}_1$  or independently are alkyl, alkenyl or aryl groups having from 1 to 10 carbon atoms.
2. A process as claimed in claim 1, characterized in that each alkyl group of the sulphoxide and/or formamide comprises from 1 to 6 carbon atoms.
3. A process as claimed in claim 1 or claim 2, characterized in that the sulphoxide is dimethyl sulphoxide or tetramethylene sulphoxide and/or that the formamide is dimethyl formamide.
4. A process as claimed in any one of claims 1 to 3, characterized in that the reaction temperature is from  $0^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ .
5. A process as claimed in any one of claims 1 to 4, characterized in that the amount of palladium catalyst is from 1 to  $10^{-6}$  molar.
6. A process as claimed in any one of claims 1 to 5, characterized in that the butadiene is contained in a butadiene/isobutene/n-butenes stream from an oil pyrolysis unit.
7. A process as claimed in any one of claims 1 to 6, characterized in that the tertiary phosphine is tri-isopropyl phosphine, tri-cyclohexyl phosphine, di-tert.-butyl-n-butyl phosphine, tri-secondary-butyl phosphine or tri-tertiary-butyl phosphine or a mixture of two or more of such phosphines.



8. A process as claimed in any one of claims 1 to 7, characterized in that the palladium catalyst is palladium acetyl acetate, palladium acetate or palladium sulphate.
9. A process as claimed in any one of claims 1 to 8, characterized in that the molar ratio of tertiary phosphine to palladium is at least 1.
10. A process as claimed in any one of claims 1 to 6, characterized in that the palladium catalyst is  $\text{Pd}(\text{R}_1\text{R}_2\text{R}_3\text{P})_2$  or  $\text{Pd}(\text{R}_1\text{R}_2\text{R}_3)_3$ , wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are as defined in claim 1.
11. A process as claimed in claim 10, characterized in that the palladium catalyst is  $\text{Pd}(\text{O})$ -tri-isopropyl phosphine.





European Patent  
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# EUROPEAN SEARCH REPORT

0008139

EP 79 200 392.3

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A, D	<u>US - A - 3 732 328</u> (D. WRIGHT) * claims 1, 3, 4, 5 *	1-3	C 07 C 11/12 C 07 C 2/08 C 07 C 2/24
A	<u>GB - A - 1 341 324</u> (I.C.I.) * claims 1, 17, 22 *	1	C 07 C 2/36 B 01 J 31/24 B 01 J 31/28
A	<u>US - A - 3 823 199</u> (D. WRIGHT) * claims 1, 6 *	1	B 01 J 37/16
A	Chemical Abstracts, vol. 85, no. 7, 16 August 1976 Columbus, Ohio, USA P. ROFFIA et al. "1,7-Octadiene" page 473, column 1, abstract no. 45941d & IT - A - 917 846 (MONTEDISON)	1	TECHNICAL FIELDS SEARCHED (Int. Cl.)  B 01 J 31/24 B 01 J 31/28 B 01 J 37/16 C 07 C 2/08 C 07 C 2/24 C 07 C 2/36 C 07 C 11/12
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search Berlin		Date of completion of the search 07-11-1979	Examiner KNAACK



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